

Temperature-dependent vibrational heterogeneities in harmonic glasses

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Numerical simulation is employed to study dynamical heterogeneities in model harmonic glasses whose atoms interact via three variants of the Lennard-Jones potential (monoatomic full Lennard-Jones, soft spheres, binary mixture). Heterogeneities are observed to exist in all three kinds of glasses, and in some cases they are observed to depend on temperature. The dimension of the heterogeneities is studied for the full Lennard-Jones case.

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The question as to whether the structure of glasses at the scale of tens to hundreds of interatomic distances is homogeneous or inhomogeneous has attracted recently much interest. Traditionally, following the continuous random network model suggested by Zachariasen [1], the homogeneous hypothesis has prevailed, also because no heterogeneity was clearly observed by small angle neutron or X-ray scattering and electron microscopy. However, these techniques show only that there is no evident density heterogeneity, but tell nothing about the cohesion or elasticity at the nanometric scale, and thus cannot rule out vibrational *dynamical* heterogeneities.

The inhomogeneous cohesion of glasses at the nanometric scale was invoked to interpret the excess of vibrational density of states in the terahertz frequency range, the so-called boson peak [2,3]. By this interpretation, the frequency of the boson peak is related to the inhomogeneity size.

Actually, recent molecular dynamics simulations on binary Lennard-Jones (LJ) mixtures [4–6] showed that in the supercooled state highly mobile and immobile particles are spatially correlated over a range that grows with temperature as the glass transition is approached; this finding is consistent with the observation of dynamical heterogeneities in supercooled liquids [7,8]. One important issue is whether or not such heterogeneities are in some sense "frozen down" through the glass transition, so that even in the cold, harmonic glass there exists a memory of these heterogeneities and, as a consequence, softer and harder zones.

In another recent simulation this problem was addressed by calculating the local pressure or stress in a glassy LJ system [9], and a strong correlation was found among atoms experiencing the same local pressure. In this reference, the elastic constants pertinent to one atom (which are related to local pressure) were determined by

keeping all the other atoms fixed [9], and if the average local elastic constant was large (small) the atom was ranked as hard (soft). Finally, very recently the vibrational modes of 2-D LJ clusters were determined numerically [10]; it was found that at length scales less than approximately 40 atomic distances the elasticity is no more affine with respect the sample deformation, and that heterogeneities of force constants are extended on the same nanometric lengths [10].

In the present paper we investigate the possible effect of temperature on the heterogeneities which are found in *harmonic* glasses of the LJ family. The existence of such effects is expected in principle on the basis of the following argument: Consider a glass at low temperature; in this case only the modes of low frequency will be excited and the atoms will only perform the cooperative motions corresponding to the normal modes in question; therefore, irrespective of the magnitude of the *local* force constants, motion in a given direction will only occur if allowed by the excitable modes. In this sense, the heterogeneities observed in Ref. [9] can describe the high-temperature behaviour, and otherwise it is expected that if disomogeneities exist, their shape, dimension, quantity etc. may depend on temperature.

We considered monoatomic systems interacting through the LJ potential ($N_0 = 2048$ atoms) or the repulsive part of the LJ potential (soft spheres, $N_0 = 2048$), and the binary LJ mixture introduced in Refs. [4–6] ($N_0 = 2000$). The potential parameters, mass and density of the LJ and soft-sphere system were those suitable for Argon [11]; for the binary mixture we chose the potential parameters as in Refs. [4–6]. The stable configurations were produced by a fast quench (down to typically $T_m/10$, where T_m is the melting temperature) of the liquid configurations starting from temperatures just above T_m . The liquid configurations were obtained by

standard MD equilibration runs. The frozen configurations at $T_m/10$ were then further equilibrated in order to check against crystallization. Finally, a steepest descent was applied to find the (glassy) minimum configuration at $T = 0$. For all systems we averaged the quantities of interest over 5 different realizations.

Following the procedure of Ref. [11], soft (hard) atoms, relative to a given eigenvector, are identified as those with small (large) variation of potential energy under the displacement pattern produced by the eigenvector itself. Therefore, in the harmonic approximation, the dynamical matrix was diagonalized, thus obtaining eigenvalues and eigenvectors. Subsequently, for each atom i and for each normal mode p , we calculated the potential-energy change due to the collective motion determined by the normal mode in question:

$$\delta V_i^p(T) = \sum_{j \neq i} V(r_{ij}^p(T)) - V(0)$$

Here the sum runs on all atoms other than i , $r_{ij}^p(T)$ is the set of atomic distances resulting from the displacements produced by normal mode p , whose amplitude depends on temperature; $V(0)$ is the potential energy of the equilibrium configuration. At a given temperature, all normal modes are excited, with amplitude depending on their energies $\hbar\omega_p$. Since the motions due to the different modes are not mutually coherent, we assume that the total potential energy variation is the sum of the weighted variations produced by the single modes:

$$\delta V_i(T) = \sum_p \delta V_i^p(T) \quad (1)$$

The distances $r_{ij}^p(T)$ can be written as $[r_i^p(T) - r_j^p(T)]$, where the atomic positions depend on the eigenvector displacements:

$$r_i^p(T) = r_i^0 + Q^p(T)e_i^p,$$

and the amplitudes Q^p are the temperature-dependent quantities. For a normal mode of frequency ω_p , and at temperature T , the average vibrational level is

$$\langle n^p(\omega_p, T) \rangle = \frac{1}{[\exp(\hbar\omega_p/kT) - 1]},$$

and the expectation value of Q^2 is calculated in the state $|n\rangle$ as:

$$Q^2 = \langle n|Q^2|n \rangle = \hbar/(m\omega_p)(2n + 1),$$

and consequently $Q^p(T) = \sqrt{Q^2}$ is determined as a function of T and ω_p , and the temperature-dependent potential-energy variations are computed through Eq. (1). In what follows, temperatures are always expressed in units of the maximum frequency ω_M of the respective systems, $T = \frac{\hbar\omega_M}{k}$.

The presence of vibrational heterogeneities is detected by comparing the normalized pair correlation function of the whole system $g_W(R)$ to that of the N softest and/or hardest atoms, $g_N(R)$ [9]; in fact, for example, if the nearest-neighbor or next-nearest-neighbor peaks in g_N are higher than in g_W it means that the N softer or harder atoms tend to group.

In Fig. 1 we report the pair correlation functions $g_N(R)$ of the monoatomic full LJ system for the $N = 20, 50, 100$ and 200 softest atoms at $T = 0.3$, and $g_W(R)$ (which is T -independent). Clear differences appear in the first peak: that of all selected groups of soft atoms is narrower, more intense than for the whole, and shifted to shorter distances, indicating that the soft atoms belong to the low- R tail. Excess correlation is observed on the next-neighbour peaks, but only for the smallest value $N = 20$, whose $g_N(R)$ is very noisy: however, the difference is so marked that such peaks might be significant.

In Fig. 2 is shown, for the same system, the temperature variation of the nearest-neighbour peak of g_N for $N = 100$, for soft (a) and hard (b) atoms. A marked temperature dependence is observed for the soft ones, together with a jump in correlation between $T = 0.1$ and $T = 0.3$. For both kinds of atoms, the peak is shifted to low R values, but for the soft ones it becomes narrower than in g_W at high T ; this can be understood by considering that the modes of low frequency, i.e. of long wavelength, are weakly dependent on the local variation of the bonding between neighbouring atoms, the dependence increases with the frequency of the modes so that the softest atoms become better differentiated from the whole. The hard atoms show little or no temperature variation on the highest point, but contrary to soft ones the overall area under the nearest-neighbour peak is increased with respect to g_W , especially at the two highest T -values.

The nearest-neighbour peaks of soft spheres are reported in Fig. 3. In this case again there is very little T -variation, but the excess correlation is quite marked across the whole peak whose area is much larger than in g_W ; the low- R side of hard atoms seems again to be favoured.

In Fig. 4 are reported the nearest-neighbour peaks for the LJ binary mixture. The major effects concern the low- R tail of the $A - A$ peak and the whole $A - B$ peak. For soft atoms, there is a strong, T -dependent increase of the former and a corresponding, T -dependent decrease of the latter. The same, but less T -independent, changes occur for hard atoms.

Summarizing the results presented so far, it can be said that for the three harmonic systems studied dynamical heterogeneities are clearly observed; the most pronounced overall correlation increases are for the binary mixture and for soft spheres, while soft inhomogeneities are observed to depend on temperature for the full LJ and binary mixture. In all cases, the most pronounced effects

concern the low- R tail of the pair correlation function.

One important question is whether with the present system size (≈ 2000 atoms) it is possible to estimate the expected size, λ , of the vibrational dynamical inhomogeneities. To check this point, in the case of full LJ we evaluated λ for samples with different number of atoms, $N_0 = 500, 1000, 1500, 2048$. In order to evaluate λ , the height of the first point of $g_N(R)$ (marked by an arrow in Fig. 2) was evaluated as a function of N and compared to the corresponding height in g_W ; the value of N at which the two become equal is taken as an estimate of the number of atoms which constitute the inhomogeneity and hence of its size. The results are reported in Fig. 5 and show that certainly for hard atoms, and probably for soft ones as well at high temperature, the heterogeneity size is still growing with N_0 at the maximum sample dimension available to us, which seems to indicate that the "true" size is larger than we can determine. One possible exception to this is the low-temperature ($T=0.01$ and 0.1) soft atoms, for which there appears to be a flattening of the curve in Fig. 5 starting at $N_0=1000$. However, before drawing definite conclusions we think it is wiser to await for more statistics (only 1 sample was examined for $N_0=500$ and 1000 , and 3 samples for $N_0=1500$). However, if the low- T result of Fig. 5 should be confirmed, temperature would play a role also in determining the soft heterogeneity size, and the same should be expected for the binary mixture (see Fig. 4(a)).

In summary, it is the first time that the existence of T -dependent vibrational dynamical heterogeneities in glasses is clearly shown to exist by simulation with LJ or soft spheres systems. However, it is not possible to draw definite and general conclusions about the heterogeneity size and its relation with the boson peak [2,3]. For that, the number of atoms in the samples studied by simulation should be much larger than 2000; work in this direction is in progress. We also plan to use other potentials taking into account long-range interactions, like for example the BKS one [12] which is suitable for SiO_2 . We expect a more contrasted inhomogeneous elasticity or vibrational inhomogeneity, like in vitreous silica, possibly in relation with a more intense boson peak [13].

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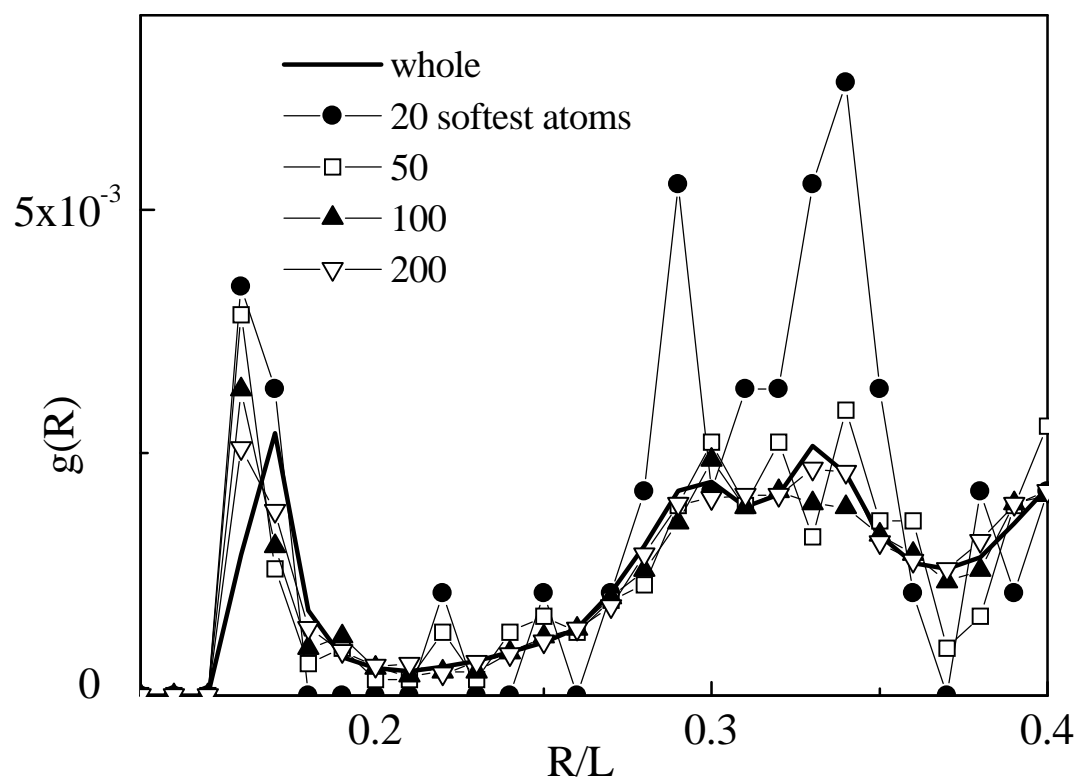
FIG. 1. Pair correlation function $g(R)$, in a monoatomic system, simulated with the full Lennard-Jones potential, for the 20, 50, 100 and 200 softest atoms compared to $g(R)$ of the whole, at $T=0.3$. L is the size of the cubic simulation box.

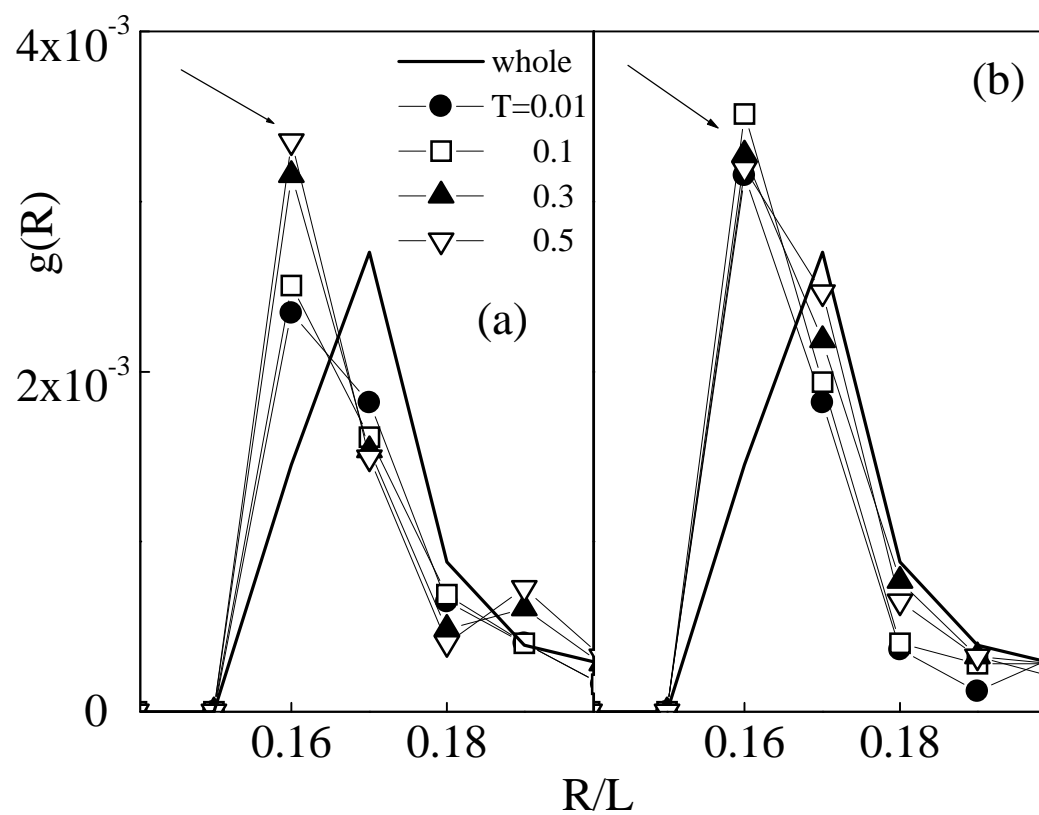
FIG. 2. Nearest-neighbour peak of $g(R)$ for the 100 softest (*a*) and hardest (*b*) atoms of the full Lennard-Jones system, at various temperatures. Arrows: see text.

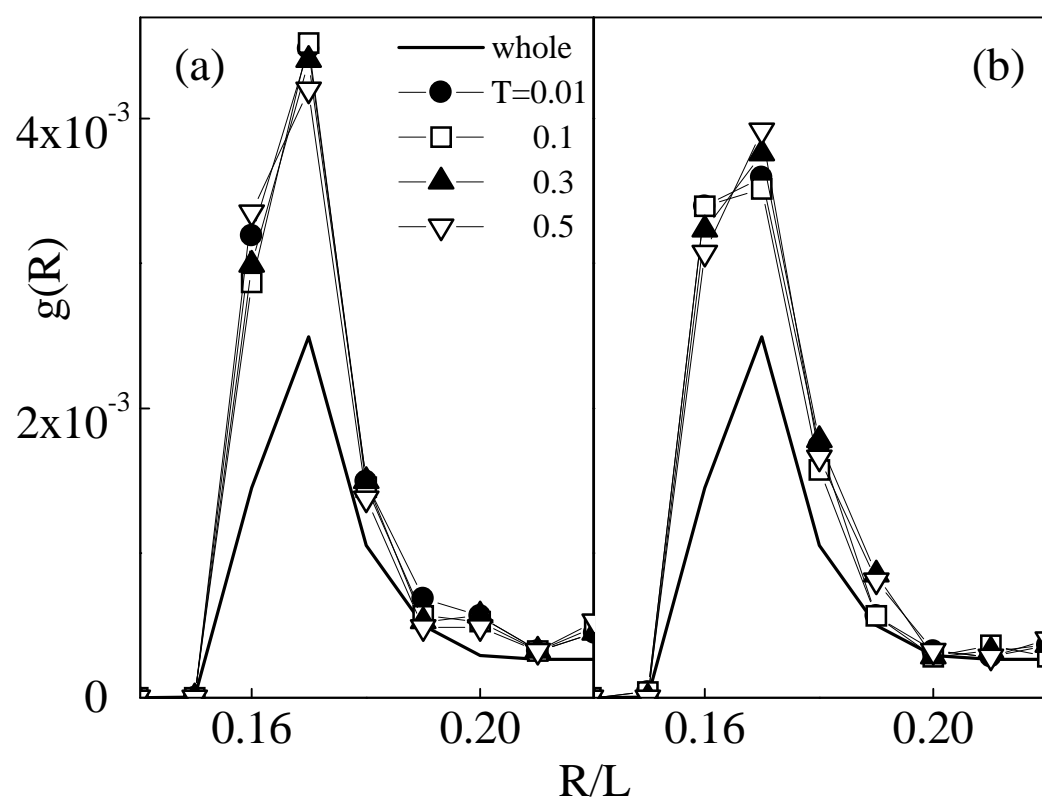
FIG. 3. Same as Fig. 2, but for soft spheres (repulsive part of Lennard-Jones).

FIG. 4. Same as Fig. 2, but for the binary $A-B$ (80%-20% respective concentration) mixture introduced in Ref. 4. The higher peak corresponds to $A-A$ neighbours, the lower one to $A-B$ ones. The $B-B$ peak is quite low and masked between the two.

FIG. 5. Dimension of hard (upper) and soft (lower) heterogeneities, evaluated as described in the text, at different temperatures, as a function of the total number of atoms in the sample (N_0). For $N_0 = 1500$ data for three different samples are reported.







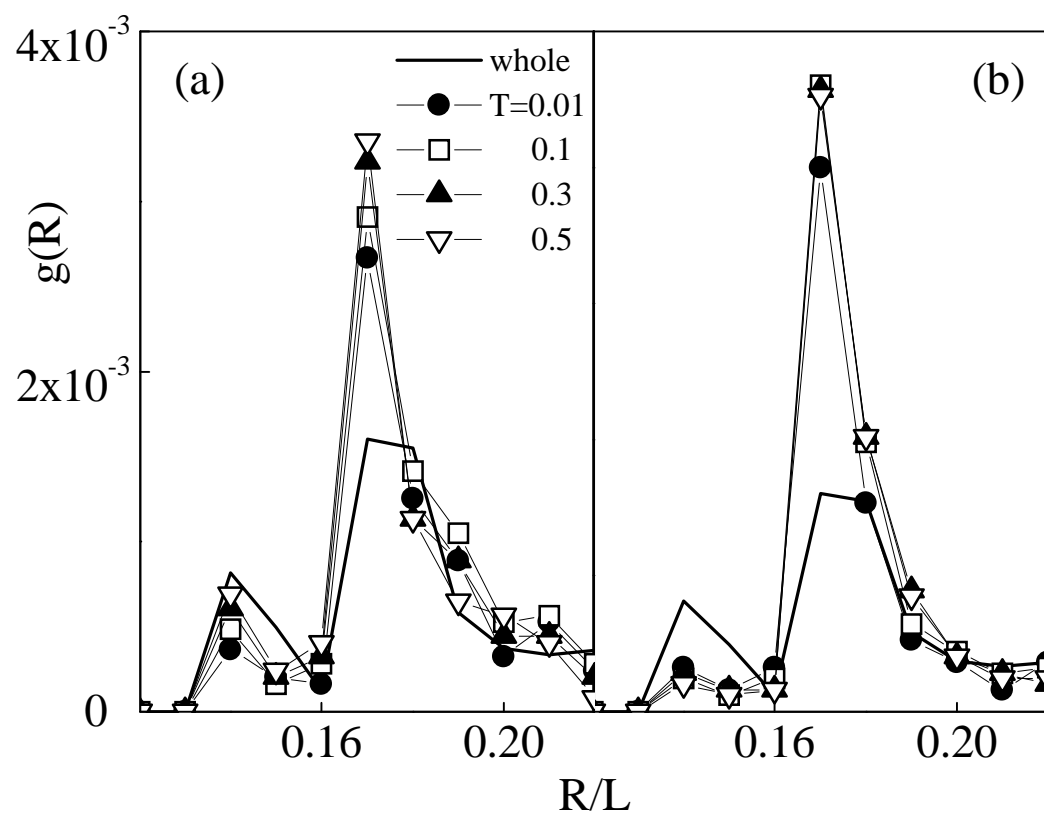


Fig 5

